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RECENT USSR WORK ON ORGANOPHOSPHORUS COMPOUNDS

 $\sqrt{\mathsf{Comment}}$: This progress report is of interest by reason of the fact that, in connection with the work of the Kazan' school on organophosphorus compounds, it refers explicitly to the strong physiological effect which certain compounds of this class can exert on warm-blooded animals 7.

A general meeting of the Department of Chemical Sciences, Academy of Sciences USSR, was held on the 75th birthday of Academician A. Ye. Arbuzov to honor this scientist.

M. M. Dubinin (Academician-Secretary of the Department of Chemical Sciences), who presided at the meeting, gave a brief introductory address in which he pointed out that A. Ye. Arbuzov has been a pioneer in research on organophosphorus compounds and must, therefore, be regarded as the founder of this subdivision of

A. Ye. Arbuzov's activity was then described more extensively in three reports, the first of which was presented by Arbuzov himself. This report, entitled "Cyclic Esters of Phosphorous Acid," revealed that new types of cyclic esters of phosphorus acid have been synthesized. Arbuzov discussed the properties of these esters as described below. These esters contain five-, six-, seven-, or eight-membered rings. The newly synthesized compounds of this type are quite reactive. When cyclic esters of phosphorous acid react with compounds of the type of alkyl halides, acyl halides, and chlorocarbonic acid ester, etc., the reaction proceeds either under fission of the ring or under retention of the ring structure. The latter property is of considerable theoretical interest.

Research in the field of chemistry under discussion has resulted in the synthesis of many compounds, some of which are of considerable practical interest. A number of compounds that belong to this class proved to be powerful agricultural insecticides. Others were found to exert a strong physiological action on warmblooded animals and for that reason promise to be of value for medical applications. Insofar as the cyclic esters of phosphorous acid are concerned, Arbuzov

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stated, the compounds of this class and the products of their conversions are merely of theoretical interest at present. In Arbuzov's opinion, however, there is no doubt that some compounds of this class will prove to be physiologically active and will, therefore, be of value for practical application.

Arbuzov's work on organophosphorus compounds, as well as that of members of his school, during the past 5 years were reviewed by B. A. Arbuzov (Corresponding Member of the Academy of Sciences USSR) as follows.

B. A. Arbuzov said that during the past 5 years intensive work on the synthesis of organophosphorus compounds has been done at the scientific institutions directed by A. Ye. Arbuzov. Sixty papers on the results of that work have been published during this time. The principal line of investigation dealt with the study of phosphorous acid esters and of the Arbuzov rearrangement of them. As a result of this study, many new organophosphorus compounds were obtained. This group of compounds includes some of an entirely new type which contain phosphorus-tim and phosphorus-silicon bonds. Considerable progress in the synthesis of phospnonic acid esters was achieved by the addition of dialkylphosphorous esters to unsaturated compounds, aldehydes, and ketones.

As early as 1930, A. Ye. Arbuzov had prepared esters of hypophosphoric acid and pyrophosphorous acid for the first time. He was the first to isolate, in a pure state, the esters of pyrophosphoric acid. These proved very effective insecticides. During the past 5 years, intensive work on organophosphorus insecticides has been conducted at the Chemical Institute of the Kazan' Affiliate, Academy of Sciences USSR.

The Chemical Scientific Research Institute imeni A. M. Butlerov at Kazan' State University has done extensive work on the investigation of complex compounds of phosphorous esters and the application of physical methods to the study of the structure of organophosphorus derivatives and other organic compounds.

B. A. Arbuzov has shown in his report that extensive research is being conducted under the direction of A. Ye. Arbuzov. He also points out that interesting results from both the theoretical and practical standpoint, may be expected in this field.

The third report, entitled "A New Method for the Synthesis of Esters of Phosphonic and Thiophosphonic Acids," was given by Prof A. N. Pudovik. In describing this method, which represents a further development of some of A. Ye. Arbuzov's ideas, Pudovik made the following observations.

The new method consists in the addition of dialkylphosphorous acids, of dialkylthiophosphorous acids, of arylphosphinous acids, and of alkylphosphinous acids to unsaturated compounds of the electrophilic type in the presence of alkaline catalysts. The addition of dialkylphosphorous and dialkylthiophosphorous acids to different alpha, beta - unsaturated ketones resulted in high yields of esters of ketophosphonic acids and ketothiophosphonic acids, whereas the addition to alpha, beta - unsaturated aldehydes led to esters of unsaturated hydroxyphosphonic and hydroxythiophosphonic acids. In the first case, addition takes place at the double bond and in the second case, at the carbonyl group.

Various esters of hydroxythiophosphonic acids were obtained by the addition of dialkylthiophosphorous acids to saturated aldehydes and ketones. Esters of phosphonocarboxylic acids were also synthesized. The addition of dialkylphosphorous acids to the esters of dibasic unsaturated acids, i.e., of maleic acid and acetylenedicarboxylic acid, led to esters of phosphonosuccinic acid and of diphosphonosuccinic acid.

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Pudovik indicated that, in the presence of alkaline catalysts, dialkyl-phosphorous acids and dialkylthiophosphorous acids add very easily to unsaturated nitriles, esters for ethers of unsaturated alcohols, ethylidenemalonic ester, benzylidenemalonic ester, acetoacetic ester, and many other compounds. By using the new method for the synthesis of phosphonic and thiophosphonic esters, more than 150 new compounds already have been obtained.

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